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(54) ANTIREFLECTION COMPOSITION AND FORMATION OF RESIST PATTERN

(57)Abstract:

PURPOSE: To obtain a compsn. which is usable as an antireflection film, allows the formation of a coating film with an aq. medium, etc., and has good step coverage even with a small film thickness by incorporating a polyvinyl alcohol(PVA) resin of a specific saponification rate into the above compsn.

CONSTITUTION: The antireflection compsn. applied between a substrate and a photoresist film contains the PVA resin having the saponification rate of  $\geq 70\%$ . This saponification rate is a value expressing the ratio of the hydroxyl group by mol%. The PVA resins having various properties by these saponification rates are known. The developer resistance at the time of, for example, developing is poor and the mixing with the photoresist film arises if the saponification rate is  $\leq 70\%$  and, therefore, such rate is undesirable. The higher saponification rate yields a better result in the developer resistance and the more preferable saponification rate is  $\geq 75\%$ . Conversely, the preservable property of the compsn. tends to degrade (leads to the production of insoluble foreign matter) if the hydrolysis rate is too high. The saponification rate is preferably  $\leq 99\%$  and further preferably  $\leq 98\%$ .

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CLAIMS

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[Claim(s)]

[Claim 1] An acid-resisting constituent characterized by containing 70% or more of polyvinyl alcohol resin whenever [ saponification ] in an acid-resisting constituent applied between a substrate and a photoresist film.

[Claim 2] The pattern-formation method characterized by to use an acid-resisting constituent according to claim 1 as this acid-resisting constituent in the pattern-formation method which includes a process which an acid-resisting constituent is applied [ process ] and makes an antireflection film form on a substrate, a process which a photoresist constituent is applied [ process ] and makes a photoresist film form on this antireflection film, the process which exposes this photoresist film and imprints a predetermined pattern on a photoresist film, and the process which develops this photoresist film using a developer.

[Claim 3] A pattern formation method according to claim 2 characterized by adding heat treatment at temperature of 110 degrees C or more after spreading of an acid-resisting constituent.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the pattern formation method using the constituent and antireflection film for forming an antireflection film in the photolithography which can be used for micro processing required for creation of a semiconductor device etc.

[0002]

[Description of the Prior Art] If the ultra-fine processing technology represented by manufacture of an integrated circuit etc. is raising the process tolerance increasingly in recent years and dynamic random access memory (DRAM) is taken for an example, in current, submicron processing technology is established as technology of mass-production-method level. The photolithography technology which used the light of short wavelength, such as g line (436nm), i line (365nm), and KrF excimer laser light (248nm), is used for this submicron processing. With such photolithography technology, although a photoresist constituent is used, amelioration is repeated also for this photoresist constituent and the constituent of high performance is examined variously (for example, JP,59-45439,A, JP,62-136637,A, JP,62-153950,A, JP,4-136860,A, JP,4-136941,A, etc.).

[0003] Although it has higher definition of course as a property required of a photoresist constituent, it important not to change the size of the imprinted pattern by the spreading thickness of a photoresist constituent. However, in photolithography, in order to be influenced of an optical interference, there was a limit in reducing size fluctuation of the pattern to fluctuation of the thickness of a resist.

[0004] That is, since the light irradiated is usually the homogeneous light, the light by which incidence was carried out into the photoresist film repeats a film Uchida pile echo by being reflected on a substrate and reflected further also on the upper surface of a photoresist film. Consequently, a periodic change took place to sensitivity to change of spreading thickness by interferential action, the measurement of the line width of the pattern imprinted further changed periodically according to fluctuation of spreading thickness, and the limit was in the dimensional accuracy of a pattern.

[0005] Moreover, when the light irradiated was reflected on the substrate, light will be irradiated by the portion of the resist which originally does not receive an optical exposure, and there was also a problem that an imprint pattern will deform as a result. Generally, since a reflection factor becomes large with short-wavelength-izing of light, the problem of an echo of the light from the above substrates poses a much more big problem by short wavelength-ization of an exposure light in recent years.

[0006] In order to reduce the echo of the light from a substrate, making an antireflection film form between a photoresist film and a substrate is known (for example, monthly Semiconductor World, the June, 1994 issue, the 83page-). Such an antireflection film is usually formed spreading and by carrying out BEKU on a substrate in the acid-resisting constituent which has sufficient absorption to exposure wavelength. A pattern is imprinted by exposure and development after forming a photoresist film on it.

(1) -- the method of etching an antireflection film selectively by the dry etching according an antireflection film to the oxygen plasma etc. by the resist film simultaneously the method of dissolving, and (2) development, after forming a resist pattern at the time of the development after exposure -- the

antireflection film is removed as be alike.

[0007] The following is mentioned as engine performance required of the antireflection film using these methods. \*\* In the method of the above (2), since a photoresist film will also be etched if etching takes long duration, also in order to shorten etching time of an antireflection film, the thinner one of the thickness is good. Therefore, it is called for that it can be used by the thinnest possible thickness as an acid-resisting constituent. \*\* Although an antireflection film needs to be uniform thickness over the whole substrate, since the substrate to be used usually has the level difference, also especially in the portion (edge section) of a level difference, the thing (step coverage is good) of the substrate which has such a level difference for which the antireflection film of the same thickness as other portions can be formed is searched for. \*\* In the method of the above (2), while it is required for a photoresist constituent that dry etching resistance should be high, an acid-resisting constituent is asked for a thing with low (dry etching nature is good) dry etching resistance. \*\* If an antireflection film and a photoresist film are mixed, in order to cause lowering of resolution, and deterioration of a pattern configuration, the photoresist constituent applied on an antireflection film and mutual are asked for dissolution mixing not being carried out (there being no mixing).

[0008] Although what is necessary is just to have thickened spreading thickness in order to have obtained the good step coverage of \*\* especially, on the other hand, the acid-resisting constituent with step coverage sufficient also when the demand of thin-film-izing of \*\* is also applied thinly for a certain reason was called for. Also in the former, the attempt used as an antireflection film by adding an extinction material to the polymer of the photoresist constituent of the existing quinone diazide system or a polyimide system, considering as an acid-resisting constituent, carrying out spreading post heating hardening and making it insolubilize had been made, and it was difficult for such an acid-resisting constituent to also solve all the above-mentioned troubles.

[0009] Moreover, in the photoresist constituent of a quinone diazide system, or the acid-resisting constituent of a polyimide system, to use organic data medium so much as data medium, and to be unable to say that he has no problem also in respect of environment, for example, to also make an antireflection film form by water data medium etc. is desired. In order to solve this problem, the acid-resisting method using a water-soluble organic compound is examined (JP,1-147535,A etc.). However, when these methods were applied to the above-mentioned method, although mixing is not caused, since this antireflection film dissolved in a developer easily at the time of the development of the photoresist film after exposure, dissolution clearance even of the antireflection film under a photoresist film will be carried out at a developer, problems, such as exfoliation disappearance of a detailed pattern, occurred, and this antireflection film was difficult [ the photoresist constituent ] for using it. Then, it can apply by water data medium etc., and is insoluble to a developer, and an antireflection film without the problem at the time of development is desired.

[0010]

[Problem(s) to be Solved by the Invention] This invention solves the above-mentioned trouble, the object can be used as an antireflection film for preventing the echo of the light from a substrate, and a spreading film can be formed by water data medium etc., and mixing with a photoresist is controlled, thin thickness also has good step coverage, and dry etching nature is to offer a good acid-resisting constituent, without this antireflection film dissolving at the time of the development of a photoresist film. Moreover, other objects of this invention have little lowering of resolution, and deformation of a resist pattern, and are to offer the pattern formation method by which change of the sensitivity by change of spreading thickness was controlled.

[0011]

[Means for Solving the Problem] When an acid-resisting constituent of engine performance which was excellent when this invention persons made polyvinyl alcohol resin of whenever [ specific saponification ] contain as a result of repeating various examination, in order to attain the above-mentioned object was obtained and an antireflection film was formed using this acid-resisting constituent, a header and this invention were reached [ that good pattern formation can be performed and ]. That is, a summary of this invention consists in an acid-resisting constituent characterized by

containing 70% or more of polyvinyl alcohol resin whenever [ saponification ] in an acid-resisting constituent applied between a substrate and a photoresist film.

[0012] Moreover, a process in which other summaries of this invention apply an acid-resisting constituent on a substrate, and an antireflection film is made to form, A process which a photoresist constituent is applied [ process ] and makes a photoresist film form on this antireflection film, In a pattern formation method which includes a process which exposes this photoresist film and imprints a predetermined pattern on a photoresist film, and a process which develops this photoresist film using a developer It consists in a pattern formation method characterized by using an acid-resisting constituent which contains 70% or more of polyvinyl alcohol resin whenever [ saponification ] as this acid-resisting constituent.

[0013]

[Embodiment of the Invention] Hereafter, it explains to details per this invention. In the acid-resisting constituent of this invention, it makes it indispensable to contain 70% or more of polyvinyl alcohol resin whenever [ saponification ]. Usually, polyvinyl alcohol resin hydrolyzes polyvinyl acetate, and the acetyl group in a polyvinyl acetate molecule is changed into a hydroxyl group, and it is manufacturing it. The value which expressed the rate of this hydroxyl group with mol % is called whenever [ saponification ], and that in which polyvinyl alcohol resin had various properties by whenever [ that saponification ] is known. For example, although polyvinyl alcohol resin is generally known as water solubility, on the other hand, whenever [ saponification / not water solubility but ] worsens at 60% or less, and whenever [ saponification ] does not dissolve vinyl acetate for the solubility to water at all substantially at less than 30%. Moreover, even if whenever [ saponification ] is too high conversely, solubility becomes low, and it has the property which 85 - 90% of thing dissolves most. In this invention, it makes it indispensable to make 70% or more of polyvinyl alcohol resin contain whenever [ saponification ] also in these polyvinyl alcohol resin. At 70% or less, for example, the developer-proof nature at the time of development worsens, and mixing with a photoresist film generates and is not [ whenever / saponification ] desirable. Moreover, whenever [ saponification ] gives a result with the higher one good [ developer-proof nature ], and is 75% or more whenever [ saponification ] preferably. Moreover, when too conversely high, it is in the inclination for the conservation stability of a constituent to worsen (generating of an insolubility foreign matter), and is [ whenever / saponification ] still more preferably [ 98% or less of ] good 99% or less.

[0014] Moreover, the polymerization degree of polyvinyl alcohol resin is expressed with aqueous solution viscosity (20 degrees C) 4%, and is usually common. [ of the thing of a 1-80cps (mPa-s) degree ] 70cps or less of polyvinyl alcohol resin used in this invention is 5cps or more usually 10cps or more and 65cps or less preferably also in this again.

[0015] Although other water soluble resin may be made to live together in this invention in the range which does not have an adverse effect on this invention, as these resin, polyacrylic acid, polyvinylpyrrolidone, a water-soluble cellulosic, etc. are mentioned. Since these resin made to live together has a possibility of spoiling the effect of this invention, it is usually good [ resin ], if there is as a content to all the solid materials in an acid-resisting constituent to carry out to 10 or less % of the weight preferably 30 or less % of the weight. [ not much much ]

[0016] The constituent of this invention usually comes to contain above-mentioned resin and water. Although the mixed activity of other organic solvents may be carried out if needed, as this solvent Isopropyl alcohol, a butanol, methoxy ethanol, ethoxy ethanol, Alcohols, such as methoxy propanol and diacetone alcohol; Ethylene glycol, glycols [ , such as propylene glycol, ]; -- dialkyl ether [ of glycols, such as dipropylene glycol wood ether ]; -- ethyl lactate -- hydroxy \*\*, such as pyruvic-acid ethyl, -- oxy-alkyl carboxylic-acid alkyl ester; -- amides, such as dimethyl formamide, dimethylacetamide, and N-methyl pyrrolidone, are mentioned. Little direction of these organic solvents is desirable, and it is usually 30 or less % of the weight preferably 50 or less % of the weight in mixture with water. Although the rate of resin to a solvent is suitably selected in consideration of spreading nature, spreading thickness, etc., it usually contains the above-mentioned resin at a rate of a degree to a solvent 0.1 % of the weight or more and 50 or less % of the weight. Among these, it is desirable to contain at a rate of a

degree especially 1 % of the weight or more and 30 or less % of the weight.

[0017] The acid-resisting constituent of this invention contains the charge of an absorber which usually absorbs the light to irradiate. As an example of these materials, a 4 and 4'-diethylamino benzophenone, A 2-hydroxy-4-benzyloxy benzophenone, 2, 2', 4, and 4'-tetra-hydroxy benzophenone, 2 and 2'-dihydroxy -4, 4'-dimethoxy benzophenone, and 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid, 2 and 2'-dihydroxy -4, 4'-dimethoxy benzophenone-5-sulfonic acid, Trimethylammonium chloride, 4-hydroxyazobenzene, (4-benzo IRUI benzyl) 4-aminoazobenzene, 4-chloro-4'-dimethylaminoazobenzene, 4-hydroxy-4'-dimethylaminoazobenzene, 4-(2'-hydroxy naphthylazo) azobenzene, 4-(3'-methyl-4'-hydroxy phenylazo) azobenzene, A 2-methyl-4-(4'-hydroxy phenylazo)-5-methoxy azobenzene, Cresol red, Methyl Red, neutral red, BUROMO Phenol Red, a Methyl Orange, a methyl yellow, a thymol blue, and Sudan III It alizarin-yellow-GG(s). sudan red <3> B, Sudan orange G, and CI- direct -- yellow 28 and CI- direct -- yellow 50 and CI- direct -- yellow 86 -- acid -- yellow 25 -- acid -- yellow 38 -- acid -- yellow 76 -- Mordant yellow 7, mordant yellow 10, and mordant yellow 12 grade are mentioned.

[0018] Although the rate of this charge of an absorber is suitably chosen by the absorbancy index of the charge of an absorber, and the thickness of an antireflection film, it is below 30 weight sections still more preferably, and is more than 5 weight sections still more preferably more than 3 weight sections preferably more than the usual 1 weight section below 40 weight sections per [ except the solvent in a constituent ] AUW (solid content weight) 100 weight section and below the usual 50 weight section.

[0019] The acid-resisting constituent of this invention can contain a surfactant further for improvement in spreading nature. The addition of this additive is suitably selected according to a desired military requirement. The acid-resisting constituent of this invention is applied between a substrate and a photoresist film, and acts as an antireflection film. After sequential spreading of an acid-resisting constituent and the photoresist constituent is carried out, a predetermined pattern is imprinted by the photoresist film by exposure, and negatives are developed with a developer.

[0020] As a photoresist constituent applied to the upper layer of an antireflection film, the constituent of various kinds of admiration radiation nature known conventionally can be used. For example, the photoresist constituent for the conventional g line, i line, and excimer laser light (248nm, 193nm) can be used, and either a positive type or a negative mold can be used as a material. As a concrete photoresist constituent, the photoresist constituent of the optical bridge formation mold of \*\* Pori cinnamic acid vinyl system and a polyisoprene cyclized-rubber system (For example, Society of Synthetic Organic Chemistry, Japan, the 42nd volume, No. 11, 979 pages), \*\* The thing which comes to dissolve 1 and 2-quinone diazide compound and alkali fusibility resin in an organic solvent Or it depolymerizes. the acid or base generated by (Society of Synthetic Organic Chemistry, Japan, 42nd volume, No. 11, 979-page, JP,62-136637,A, JP,62-153950,A, etc. and \*\*s) light exposure -- a polymerization -- [ for example, ] The so-called chemistry amplification mold photoresist constituent (for example, JP,59-45439,A, JP,4-136860,A, JP,4-136941,A) which discovers the engine performance of admiration radiation nature is mentioned.

[0021] \*\* As resin used for a photoresist constituent, polyvinyl alcohol, the Pori cinnamic acid vinyl system resin manufactured from cinnamic acid chloride, and the cyclized-rubber system resin which uses 1 and 4-cis- polyisoprene as a principal component are mentioned. To these resin, photoinitiator cross linking reagents, such as a 4 and 4'-diazido chalcone and 2 and 6-G (4'-azide benzylidene) cyclohexanone, may be added if needed.

[0022] \*\* As a 1 and 2-quinone diazide compound used for a photoresist constituent, a 1 of compound which has hydroxyl group of phenol nature, 2-benzoquinone diazido-4-sulfonate derivative, 1, 2-naphthoquinonediazide-4-sulfonate derivative, 1, and 2-naphthoquinonediazide-5-sulfonate derivative etc. is mentioned. Here, as a compound which has a phenolic hydroxyl group, polyhydroxy benzoates, such as polyhydroxy benzophenones, such as 2, 3, and 4-trihydroxy benzophenone, and gallic-acid ethyl, the polyphenol like bisphenol A manufactured from phenols and carbonyl compounds, novolak resin, etc. are mentioned. Moreover, the polymer to which the novolak resin to which the polycondensation of a phenol derivative and the aldehyde derivative was carried out, an acrylic-acid

derivative, a cinnamic acid derivative, a styrene derivative, a maleic-acid derivative, etc. were made into the monomer as alkali fusibility resin used for the photoresist constituent of \*\*, and the polymerization of these was carried out is mentioned.

[0023] \*\* It consists of resin which has an unstable radical to acids, such as Pori (p-tert-butoxycarbonyloxy) styrene, as a photoresist constituent, and a compound which generates an acid by the optical exposure of triphenylsulfonium hexafluoroacetate etc., and the photoresist constituent which the optical exposure section solubilizes or insolubilizes to a developer is mentioned (for example, JP,59-45439,A). Moreover, it consists of novolak resin to which the polycondensation of a phenol derivative and the aldehyde derivative was carried out, and a compound which generates an acid by the optical exposure of cross linking agents, such as an alkoxy methylation melamine and an alkoxy methylation urea, halogenation methyl triazine, etc., and the photoresist constituent which the optical exposure section insolubilizes to a developer is mentioned. (For example, JP,4-136860,A, JP,4-136941,A) .

[0024] Although a photoresist constituent usually contains an organic solvent As an organic solvent, for example Acetic-ester; ethylcellosolve [, such as aromatic hydrocarbon; ethyl acetate, ], such as toluene and a xylene, etc., Monochrome, monochrome of a diethylene glycol, or dialkyl ether; Propylene glycol monomethyl ether etc., monochrome, the monochrome of dipropylene glycol, or dialkyl ether; -- alkyl cellosolve acetate [, such as propylene-glycol-monomethyl-ether acetate, ]; -- ethylene carbonate -- Ester, such as gamma-butyrolactone; as for alkoxy \*\*, such as ketones; ethyl lactates, such as a methyl ethyl ketone, 2-heptanone, and cyclopentanone, 3-methoxy methyl propionate, and pyruvic-acid ethyl, oxy-alkyl carboxylic-acid alkyl; etc. is mentioned. These solvents are suitably chosen in consideration of solubility, such as resin and a sensitization agent, the stability of a photoresist constituent, etc.

[0025] Moreover, these photoresist constituents can also contain the surfactant for spreading nature amelioration, the sensitizer for the improvement in sensitivity, etc. if needed. Although there is especially no limit as a substrate used for pattern formation, substrates for IC manufacture, such as a silicon substrate and a gallium arsenide substrate, are common, and that by which the layer with high reflection factors, such as aluminum, is formed in the front face is also mentioned.

[0026] There is especially no limit in the method of applying an acid-resisting constituent on a substrate, and the method of applying a photoresist constituent on an antireflection film, a spin coater etc. is used, and it is carried out according to a conventional method. Although the applied acid-resisting constituent is heat-treated using a hot plate etc. and usually removes a solvent, the water resisting property of the antireflection film formed when this temperature was not much low will not improve, but an antireflection film will also be dissolved at the time of development, and it is not desirable. Moreover, it becomes [ if this temperature is too high not much, will cause disassembly of polyvinyl alcohol, and ] the cause of generating of particle and is not desirable. They are 115 degrees C or more and 240 degrees C or less often [ the heat treatment temperature for obtaining the good water resisting property of an antireflection film / carrying out below 110 degrees C or more and 260 degrees C ], and preferably. Moreover, if nearby optimum ranges differ in the class of polyvinyl alcohol to be used and whenever [ optimal saponification / of said polyvinyl alcohol ] is included, this heat treatment temperature In the range at the time of expressing whenever [ saponification / of polyvinyl alcohol ], and heat treatment temperature with a two-dimensional graph The conditions of the range surrounded in respect of Point A (whenever [ saponification ] 70%, heat treatment temperature of 160 degrees C), Point B (whenever [ saponification ] 70%, heat treatment temperature of 240 degrees C), Point C (whenever [ saponification ] 100%, heat treatment temperature of 260 degrees C), and Point D (whenever [ saponification ] 100%, heat treatment temperature of 110 degrees C) are desirable. Preferably Furthermore, the point E (whenever [ saponification ] 75%, heat treatment temperature of 170 degrees C) Point F (whenever [ saponification ] 75%, heat treatment temperature of 230 degrees C), Point G (99% whenever [ saponification ]) The conditions of the range surrounded in respect of the heat treatment temperature of 240 degrees C and Point H (whenever [ saponification ] 99%, heat treatment temperature of 115 degrees C) are desirable. Most preferably The conditions of the range surrounded in respect of Point E (whenever [ saponification ] 75%, heat treatment temperature of 170 degrees C), Point I (whenever [ saponification ] 75%, heat treatment temperature of 200 degrees C), Point J (whenever

[ saponification ] 98%, heat treatment temperature of 200 degrees C), and Point K (whenever [ saponification ] 98%, heat treatment temperature of 120 degrees C) are good. Moreover, heat treatment time amount is usually 30 seconds or more and 600 seconds or less, and is 60 seconds or more and 300 seconds or less preferably.

[0027] While the constituent of this invention can be applied again at the time of spreading so that step coverage may become good by the comparatively thick film since contraction by the time of heat treatment is larger than the conventional thing, by subsequent heat treatment, it can shrink a film and can obtain the antireflection film of thin thickness eventually. Consequently, if the acid-resisting constituent of this invention is used, step coverage can make the antireflection film of good and thin thickness form. In order to obtain the good water resisting property of an antireflection film, the aforementioned heat treatment temperature is enough below 200 degrees C, but in order [ this ] to make it contract greatly and to obtain the antireflection film of thin thickness, it can also heat-treat at a further 220-260-degree C elevated temperature to an elevated temperature, for example, 200-220 degrees C, further. However, since polyvinyl alcohol decomposes in heat treatment of an elevated temperature and long duration and a film deteriorates, it is not so desirable.

[0028] In addition, even if it performs the above-mentioned heat treatment in the constituent of this invention, dry etching nature is good as compared with novolak resin, polyimide resin, etc. (Dry etching resistance is low.)

Thus, although the thickness of the antireflection film obtained changes with demands from the concentration of the extinction agent in an antireflection film, and a photolithography process etc., it is usually about 0.1-1 micrometer about 0.05-2 micrometers.

[0029] About the method of application of the photoresist constituent after antireflection film formation, the exposure method, and the development method, well-known various methods are conventionally employable. The thickness of the applied photoresist constituent is usually about 0.3-5 micrometers. Moreover, stoving processing may be performed after spreading of a photoresist constituent, and it is usually carried out for 30 - 120 seconds at 70-130 degrees C using a hot plate etc.

[0030] As exposure wavelength used for performing an image imprint on the formed photoresist film, g line (436nm), i line (365nm), XeCl excimer laser light (308nm), KrF excimer laser light (248nm), ArF excimer laser light (193nm), etc. are usually effective. Exposure afterbaking (PEB) may be performed after exposing a photoresist film if needed. The conditions for about 60 - 120 seconds are suitably used at 70-130 degrees C, using a hot plate etc. as conditions for PEB. Although a convection oven may be used instead of a hot plate, time amount longer than the case where a hot plate is usually used in this case is needed.

[0031] As a developer for developing a photoresist after exposure An alkali aqueous solution is used. Usually, for example, a sodium hydroxide, a potassium hydroxide, Inorganic alkali, such as a sodium carbonate, aqueous ammonia, a sodium silicate, and a meta-sodium silicate Primary amines, such as ethylamine and n propylamine, diethylamine, Tertiary amines, such as secondary amines, such as G n propylamine, triethylamine, and methyl diethylamine What added alcohol etc. is mentioned to aqueous solutions, such as quarternary ammonium salt, such as tetramethylammonium hydroxide and trimethylhydroxyethylammonium hydroxide, or this. Moreover, a surfactant etc. can also be added and used if needed. About 15-30 degrees C of developing time are [ development temperature ] desirable about 30 to 180 seconds. In addition, a developer is filtered on the occasion of an activity, and it is usually used for it for insoluble matter, removing.

[0032]

[Example] Although an example is given and this invention is explained further below at details, this invention is not limited to these examples at all, unless the summary is surpassed. In addition, especially the handling of the photoresist constituent of the following examples was performed in the clean room of the class (the so-called yellow room) 100 using the fluorescent lamp which shaded light 500nm or less, when [ all ] there was no explanation.

[0033] (Example 1) 1.4g of tetramethylammonium salts of polyvinyl alcohol (whenever [ Nippon Synthetic Chemical Industry Co., Ltd. make, GH-20, and saponification ]; 86.5 - 89.0%) 5.1g and 5-(3'-

nitro phenylazo) salicylic acid (alizarin yellow GG) was dissolved in 93g of water. This was filtered with the membrane filter of 0.2 micrometers of apertures, and the acid-resisting constituent A was prepared.

[0034] On the other hand, in m-cresol, p-cresol and 2, and 5-xyleneol (mole ratio = 5:4:1) list 14.0g (average molecular weight 3,500) of cresol system novolak resin compounded from formaldehyde and an acetaldehyde (mole ratio = 8:2), 7.3g (40% of rates of average esterification) of admiration illuminants compounded from the novolak resin (average molecular weight 1,000) compounded from m-cresol and an acetaldehyde, and 1 and 2-naphthoquinonediazide-5-sulfonic acid chloride It dissolved in 56g of 3-methoxy methyl propionates. This was filtered with the membrane filter of 0.2 micrometers of apertures, and the photoresist constituent A was prepared.

[0035] After applying this acid-resisting constituent A by the spin coater on the silicon wafer which carried out sputtering of the aluminum to 0.2 micrometers in thickness, it baked on the hot plate for 60 seconds at 180 degrees C, and the antireflection film of 0.2-micrometer thickness was made to form. After applying the photoresist constituent A by the spin coater similarly further, it baked on the hot plate for 90 seconds at 80 degrees C, and the photoresist film of 1.07-micrometer thickness was made to form on this antireflection film.

[0036] The result of having investigated the situation of mixing with the antireflection film and photoresist film which were obtained is shown in a table -1. This wafer was exposed according to the conventional method using i line stepper (NIKON CORP. make NA=0.5), and PEB (for 110 degrees C and 90 seconds) and development (they are an activity, 23 degrees C, and 60 seconds about the 2.38 % of the weight aqueous solution of tetramethylammonium hydroxide) were performed.

[0037] The result of having observed the cross-section configuration of the imprinted pattern in the light exposure to which a 0.5-micrometer line & space is finished in 1:1 using the electron microscope is shown in a table -1. Moreover, at this time, dissolution clearance was not carried out at the time of development, but the antireflection film remained. It applied by the spin coater and the antireflection film of 0.20-micrometer thickness was made to form on the silicon wafer which, on the other hand, has the pattern which has the level difference of 1 micrometer in the acid-resisting constituent A.

[0038] This antireflection film was baked on the hot plate for 600 seconds at 200 more degrees C. The thickness of the obtained film was measured, and reduction of the thickness by heat treatment was investigated, and the situation of the step coverage of the level difference section at this time was investigated. A result is shown in a table -1. The heat-treated wafer with an antireflection film whose thickness obtained by the same method as the above further again is 0.5 micrometers, After applying the photoresist constituent A to a silicon wafer by the spin coater like the above, The wafer with a photoresist film baked and obtained on the hot plate for 90 seconds at 80 degrees C Dry etching prepare, respectively and according to the oxygen plasma of these spreading films (the pressure of 15Pa) RF power 300W, etching gas The speed of oxygen was measured and it asked for the etching velocity ratio (etch rate of the etch rate / photoresist film of an antireflection film) of an antireflection film and a photoresist film. A result is shown in a table -1.

[0039] (Example 2) Polyvinyl alcohol (whenever [ Wako Pure Chem make, polymerization-degree about 2000 weight average molecular weight 88,000, and saponification ] 78 - 82%) 4.8g and 1.2g monohydrates) (SHIPRO formation Make, SEESORB 101 S) of 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid were dissolved in 94g of water. This was filtered with the membrane filter of 0.2 micrometers of apertures, and the acid-resisting constituent B was prepared.

[0040] On the other hand, the partial t-butoxycarbonyl ghosts 20g and 2 of a polyvinyl phenol (the Maruzen Petrochemical [ Co., Ltd. ] make, weight average molecular weight: 5,200), 8.6g of t-butoxycarbonyl ghosts of 6-screw (2-hydroxy-5-methylbenzyl)-4-methyl phenol, and triphenylsulfonium triflate (Green Chemistry company make) 1.4g were dissolved in diethylene-glycol wood ether 78g.

[0041] This was filtered with the membrane filter of 0.2 micrometers of apertures, and the photoresist constituent B was prepared. After applying this acid-resisting constituent B to a silicon wafer by the spin coater, it baked on the hot plate for 300 seconds at 200 degrees C, and the antireflection film of 0.2-

micrometer thickness was made to form. After applying said photoresist constituent B by the spin coater similarly further on this antireflection film, it baked on the hot plate for 90 seconds at 120 degrees C, and the wafer with a photoresist film was obtained. Under the present circumstances, two or more wafers are prepared and it was made to become the thickness to 0.9 to 1.05 micrometers at intervals of about 0.01 micrometers.

[0042] The result of having investigated the situation of mixing with the antireflection film and photoresist film which were obtained is shown in a table -1. The obtained wafer was exposed according to the conventional method using the excimer laser stepper (the NIKON CORP. make, NA=0.42) (KrF excimer laser), and PEB (for 80 degrees C and 90 seconds) and development (they are an activity, 23 degrees C, and 60 seconds about the 2.38 % of the weight aqueous solution of tetramethylammonium hydroxide) were performed.

[0043] 2mm angle extracted and the photoresist film of a pattern measured the minimum light exposure (Eth) taken to develop and remove even a substrate. As mentioned above, although this sensitivity changed periodically with change of photoresist thickness, it measured 0.93 micrometers of photoresist thickness in this case, and a 1.00 micrometers (it is equivalent to the mountain of the above-mentioned period, and a valley) sensitivity ratio [Eth / 1.00 micrometers [ of 0.93 micrometers / of thickness / thickness ] Eth]. A result is shown in a table -1. Moreover, like the example 1, reduction of the thickness by heat treatment of the antireflection film of 0.2-micrometer thickness was investigated, and the situation of the step coverage of the level difference section at this time was investigated. A result is shown in a table -1.

[0044] (Example 3) Except having replaced polyvinyl alcohol with the thing (whenever [ H-20 and saponification ] 95.0 - 96.0%) by DENKI KAGAKU KOGYO K.K. from the Wako Pure Chem thing, the acid-resisting constituent C was prepared like the example 2, and 0.93 micrometers of photoresist thickness and a 1.00-micrometer sensitivity ratio were measured like the example 2 below. A result is shown in a table -1.

[0045] (Example 1 of a comparison) The cross-section configuration of the imprinted pattern in the light exposure to which a 0.5-micrometer line & space is finished in 1:1 was observed like the example 1 except having not applied an acid-resisting constituent. A result is shown in a table -1.

(Example 2 of a comparison) 0.93 micrometers of photoresist thickness and a 1.00-micrometer sensitivity ratio were measured like the example 2 except having not applied an acid-resisting constituent. A result is shown in a table -1.

[0046] 7.6g (average molecular weight 12,000) of cresol system novolak resin compounded from formaldehyde in m-cresol and a p-cresol (mole ratio = 6:4) list, (Example 3 of a comparison) Pyrogallol, the novolak resin (average molecular weight 1,300) compounded from the acetone, and 1, 0.13g (50% of rates of average esterification) of admiration illuminants compounded from 2-naphthoquinonediazide-5-sulfonic acid chloride, And 4-(3'-methyl-4'-hydroxy phenylazo) azobenzene (Mitsubishi Chemical make) 2.5g was dissolved in 90g of 3-methoxy methyl propionates. This was filtered with the membrane filter of 0.2 micrometers of apertures, and the acid-resisting constituent D was prepared.

[0047] The situation of mixing with an antireflection film and a photoresist film (photoresist constituent A) and the cross-section configuration of the imprinted pattern in the light exposure to which a 0.5-micrometer line & space is finished in 1:1 were investigated like the example 1 except having replaced with and used this acid-resisting constituent D for the acid-resisting constituent A, and having replaced the heat treatment conditions after applying the acid-resisting constituent D with in 600 seconds at 250 degrees C. A result is shown in a table -1. Moreover, at this time, dissolution clearance was not carried out at the time of development, but the antireflection film remained.

[0048] Moreover, like examples 1 and 2, reduction of the thickness by heat treatment was investigated, and the situation of the step coverage of the level difference section at this time was investigated. A result is shown in a table -1. Reduction of the thickness by heat treatment and the situation of the step coverage in the level difference section were similarly investigated further again except having set thickness in early stages of an antireflection film to 0.20 to 0.13 micrometers. A result is shown in a table -1. It asked for the etching velocity ratio of an antireflection film and a photoresist film like the

example 1 further again except having replaced the antireflection film A with the antireflection film D. A result is shown in a table -1.

[0049] (Example 4 of a comparison) Exposure and development were performed like the example 1 except having replaced polyvinyl alcohol with the pullulan (made in Hayashibara). When the pattern imprinted with the optical microscope after development was observed, most separated and the pattern 1.0 micrometers or less had disappeared.

(Example 5 of a comparison) Exposure and development were performed like the example 1 except having replaced the acid-resisting constituent A with the acid-resisting constituent D. When the pattern imprinted with the optical microscope after development was observed, the antireflection film and the photoresist film have caused mixing and resolution, a pattern configuration, etc. were farther [ than the example 1 of a comparison which did not use the acid-resisting constituent A ] inferior.

[0050]

[A table 1]

表 - 1

	反 射 防 止 組成物	フォトリソ膜とのミッシング	パターンの断面形状	熱処理による膜厚の減少 (膜 厚 0.20 $\mu$ m)	ステップカバレッジ (膜 厚 0.20 $\mu$ m)	エッチング速度比	感度比	熱処理による膜厚の減少 (膜 厚 0.13 $\mu$ m)	ステップカバレッジ (膜 厚 0.13 $\mu$ m)
実施例 1	A	ミッシング せず	アンダーカット なく、良好	0.11 $\mu$ m	良 好	1.5 以上	—	—	—
実施例 2	B	ミッシング せず	—	0.12 $\mu$ m	良 好	—	1.03	—	—
実施例 3	C	ミッシング せず	—	—	—	—	1.03	—	—
比較例 1	なし	—	アンダーカット あり	—	—	—	—	—	—
比較例 2	なし	—	—	—	—	—	1.26	—	—
比較例 3	D	ミッシング せず	アンダーカット なく、良好	0.15 $\mu$ m	良 好	1	—	0.10 $\mu$ m	不 良

[0051] In addition, in a table -1, the existence of an undercut shows the existence which goes away near a substrate and in which it is that it is crowded (undercut) in the resist pattern obtained after development. This situation is shown in drawing 1 . Drawing 1 is the typical cross section showing a resist pattern, and (a) does not have an undercut and shows the condition that (b) has an undercut in a good condition, respectively. To the photoresist 11 maintaining the rectangle on a substrate or an antireflection film 12, it is hard photoresist 11, is crowded with drawing 1 (b) in near a substrate or an antireflection film 12, at drawing 1 (a), and is \*\*\*\*\*.

[0052] Moreover, drawing 2 is the typical cross section showing the quality of step coverage. In drawing 2 , (a) shows a condition with good step coverage, and (b) shows a defect's condition, respectively. In drawing 2 (a), the antireflection film 20 formed on the substrate 21 which has a level difference is formed by uniform thickness also in the level difference section. On the other hand in drawing 2 (b), the antireflection film 20 formed on the same substrate 21 does not become uniform thickness in the level difference section, and the edge is not fully covered.

[0053]

[Effect of the Invention] The amount of organic data medium used which poses a problem in respect of environment according to this invention can form an antireflection film good at least, it can be used as an antireflection film for preventing the echo of the light from a substrate, mixing with a photoresist is controlled, and dry etching nature can offer a good acid-resisting constituent good [ thin thickness / step coverage ]. Moreover, there are little lowering of resolution and deformation of a resist pattern, and the

pattern formation method by which change of the sensitivity by change of spreading thickness was controlled can be offered.

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[Translation done.]

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] The typical cross section showing a resist pattern.

[Drawing 2] The typical cross section showing the quality of step coverage.

[Description of Notations]

11 Photoresist

20 Antireflection Film

21 Substrate

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[Translation done.]

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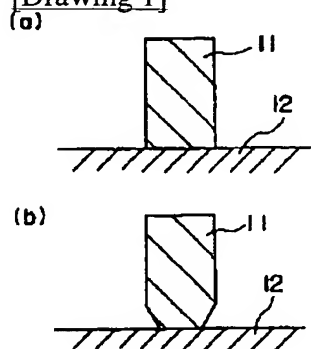
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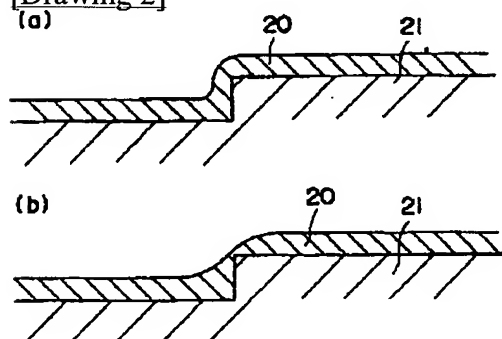
DRAWINGS

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[Drawing 1]



[Drawing 2]



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[Translation done.]